UNIVERSITY OF TARTU
Faculty of Science and Technology
Institute of Technology

Jelena Volobujeva

Deep Eutectic Solvents as Electrolytes in Ionic Electromechanically Active Polymer Actuators

Bachelor's Thesis (12 ECTS)

Curriculum Science and Technology

Supervisors:
MSc Fred Elhi
PhD Kaija Põhako-Esko

Tartu 2019

Deep Eutectic Solvents as Electrolytes in Ionic Electromechanically Active Polymer Actuators

Abstract:

In the twenty-first century, electroactive polymer actuators have found new application as artificial muscles. Previously, the bending efficiency was in the priority, that is why ionic liquids have been used as electrolytes for such type of actuators, though it was known that they are a hazard for living organisms. Since these artificial muscles are planned to be used in medical devices and human bodies, it is essential that actuators should be bio-friendly and prepared from low-toxic materials. That is why a new type of choline-based deep eutectic solvents has been tested in the current study as electrolytes for actuators. Such electrolytes could be prepared from inexpensive and low toxic materials. Additionally, in comparisons to ionic liquids, they show comparable results in displacement and exceed in capacitor like behavior.

Keywords:

Ionic electromechanically active polymer actuators, conductive polymers, polypyrrole, ionic liquids, deep eutectic solvents

CERCS: T150 material technology

Eutektilisete segude kasutamine elektrolüütidena ioonsetes elektromehaanliselt aktiivsetes polümeersetes täiturites

Lühikokkuvõte:

Elektroaktiivsed polümeerid on 21. sajandil leidnud laialdast tähelepanu tänu võimalusele kasutada neid tehislihastes. Varasemalt pöörati tähelepanu peamiselt nende materjalide liikumisamplituudi suurendamisele ning leiti, et ioonsete vedelike kasutamine elektrolüüdina aitab sellele kaasa. Elektroaktiivsete polümeersete täiturite üheks rakendusvaldkonnaks on mitmesugused meditsiiniseadmed, mistõttu on oluline välja töötada bioühilduvad materjalid. Traditsiooniliste ioonsete vedelike toksilisuse tõttu otsitakse neile käesolevas töös biosõbralikku alternatiivi. Testiti koliini baasil ioonseid vedelikke ja eutektilisi segusid kui madala toksilisusega elektrolüüte elektroaktiivsete polümeersete täiturite jaoks. Ioonsete vedelike ja eutektiliste segude võrdlusest selgus, et testitud süsteemides võib eutektilisi segusid kasutada asendamaks ioonseid vedelikke.

Võtmesõnad:

Ioonsed elektroaktiivsed polümeersed täiturid, juhtivpolümeerid, ioonsed vedelikud, polüpürrool, eutektilised segud

CERCS: T150 materjalitehnoloogia

TABLE OF CONTENTS

TERMS, ABBREVIATIONS AND NOTATIONS

Bp – boiling point

[Ch][AC] – choline acetate ionic liquid

[Ch]Cl – choline chloride

[Ch]Cl:AA – DES formed from choline chloride and acetic acid

[Ch]Cl:LA – DES formed from choline chloride and lactic acid

[Ch][LA] – choline lactate ionic liquid

CP – conductive polymer

CV – cyclic voltammetry

DES – deep eutectic solvents

EAP – electroactive polymers

EW – electrochemical “window”

IEAP – ionic electromechanically active polymers

IL – ionic liquid

IR – infrared

Mp – melting point

MW – molar weight

NMR – nuclear magnetic resonance

PPy – polypyrrole

PVDF – polyvinylidene fluoride

RTIL – room-temperature ionic liquid

ρ – density

INTRODUCTION

In recent years science and engineering are moving towards soft robotics and bioinspired systems. Therefore, the importance and applications of ionic electromechanically active polymer (IEAP) actuators have rapidly increased. These devices have several advantageous properties: lightness, simplicity, microscale size, which make them attractive for the developing sphere.

The bending of IEAP actuators is caused by the movement of ions in solution between electrodes. Since the effectiveness, life-time and strain difference of laminates are strongly depended on the electrolytes, it is necessary to properly choose the solvent.

During last years the main electrolyte for this purpose was ionic liquids (ILs), due to their promising electrochemical properties and negligible vapour pressure. One commonly used type of such electrolytes are imidazole based ILs. Previous investigations have discovered the superiority of new solvents over the classical salt solutions: longer life-time, environmental stability.[1] However, later it was analysed that these ILs are toxic for living organisms.

Since nowadays more attention has been paid to the bio-friendliness and safety of the materials and more researches are devoted to the use of actuators in the human body: blood vessel connectors, cochlear implants,[2] it is essential to have well characterized and low-toxic compounds. Not all ILs meet this requirement, that is why these ILs are needed to be replaced with safer alternatives, though, with similar electrochemical properties and minimal lose in the effectiveness.

A new type of solvents, known as deep eutectic solvents (DES), could be formed from natural and biodegradable materials, they satisfy safety standards and share several properties of previous solvents. Such characteristics make DES prospective substitute to ILs.

This thesis is concentrated on choline based ILs and DES formed from [Ch]Cl. Both electrolytes contain choline cations and have similar chemico-physical properties. The main purpose of the work is to investigate the behaviour of polypyrrole (PPy) actuators with a new type of electrolytes and check the hypothesis, whether DESs are comparable alternatives to ILs solvents in IEAP actuators.

1 LITERATURE REVIEW

1.1 Electroactive polymers

Electroactive polymers (EAP) are one type of intelligent materials, which are capable of performing the mechanical deformations in the response to applied electrical signals.

These laminates have characteristics features such as light weight, softness, option to be fabricated at the microscale and silence. That is why, EAPs have found application in the field of biomimetics as sensors and actuators[3], which could mimic properties of living creatures' muscles.[4]

In recent years the numerous amounts of EAP technologies have been explored for biomimetic actuation, however, several of them are still too toxic for being used in living organisms.[2] That is why, the great interest of modern researches is paid to the creation of actuators from bio-friendly and low toxic compounds, which could be used in personal assisting devices and medical implants without harm and risks to human body and health.[5]

Based on the mechanism of actuation these polymers can be divided into electronic and ionic EAPs (IEAP). In case of electronic EAPs, the polymers are driven by coulomb forces or electric field and unlike IEAP does not require electrolytes.[4] Though, this type of polymers have several disadvantages: high activation voltages (~150 MV/m), which are close to the material breakdown limits[4] and concord between strain and stress.[6]

The main interest of this thesis will be paid to ionically active EAPs.

1.1.1 Ionic electroactive polymers

IEAPs consist of three main elements: electrodes, a separating membrane and an electrolyte (Figure 1).[7] Conducting polymers (CP), different carbon allotropes and metals can be used as the materials for the electrodes in IEAP.

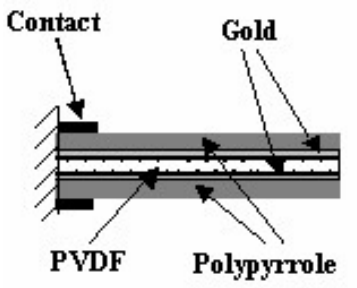


Figure 1. Schematics of IEAP, where PVDF – porous separating membrane drowned in the electrolyte, polypyrrole – CP used as electrodes.[8]

The reason for the bending of IEAP actuators is volume changes, which are caused by ionic motion through the porous dielectric layer between electrodes. For example, in case of conductive polymer electrodes in the process of electrochemical oxidation, the charge is removed from polymer chains. For neutralization of the polymer structure, ions from the electrolyte are transferred in or out of the polymer.[9]

IEAP actuators can be anion- or cation- driven, dependent on what kind of charged particles will cause the volume expansion. If it is anion-driven actuator, the anions from the surrounding electrolyte move into the positively charged polymer, this side expands, and the bending direction is from the positive to the negative electrode. In the case of cation - driven as shown in Figure 2, the positively charged particles are reversibly pushed out from the positive electrode causing this side to shrink.[8]

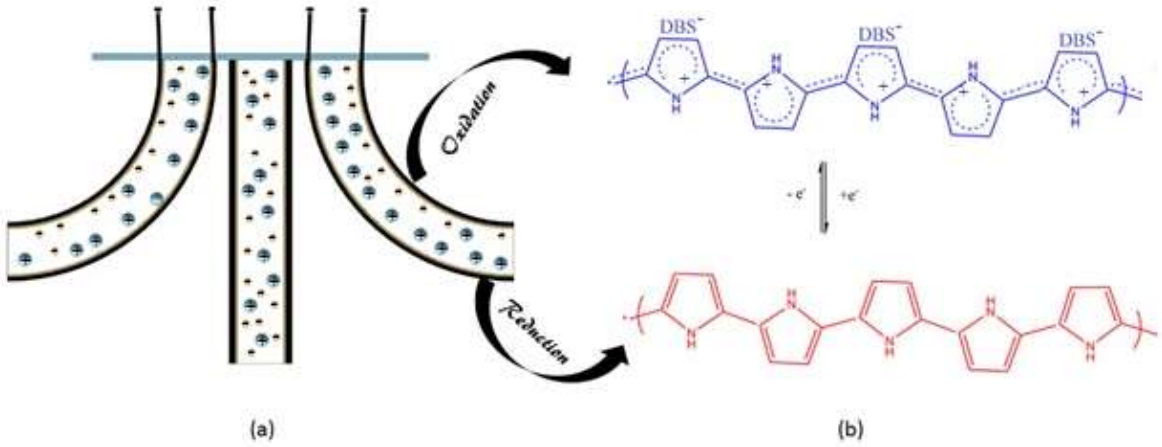


Figure 2. Schematics of ions move and actuator behaviour in the process of a redox reaction, in the example of PPy (a) IEAP actuator bending (b) oxidation and reduction of the polymer backbone. Adapted from:[10]

The flow of ions and consequently the amount of volume change depends on the size of particles, conductivity, a thickness of the membrane, scan rate and amount of applied voltage.[11] IEAP actuators are relatively easy to control as the displacement is proportional to the number of relocated ions.[5]

Due to several attractive properties: high strength, ability to work at body temperature and low working voltage (in the range of 2V), IEAP actuators could be used in the body of living organisms[2,12] So that in the research work of E. Jager, E., E. Smela, O. Inganas was shown that PPy/Au based actuators can be used for grabbing small objects like nerve or nerve fibers.[12] Additionally, E.Smela in cooperation with several research groups have developed conducting polymers for the application as blood vessel connectors, cochlear implants and microvalve for controlling the urinary incontinence.[2]

1.1.1.1 Conductive polymers

Conductive also known as π-conjugated polymers are organic compounds, which are capable of electricity conducting. These conductive properties of CP are caused by structure of polymer with overlapping π-orbitals in the repeating pattern of single and double carbon bonds in the backbone.[13]

Among several CP the best known and commonly used are: polypyrrole (PPy) (conductivity up to 50 S/cm), polyaniline (conductivity up to 10^2 S/cm), polyacetylene (conductivity up to 10^5 S/cm).[14] Such polymers are one of the possible materials for IEAP electrodes, which can be used for low voltage (1-5 V) electrochemical actuators with large stress (up to 34 MPa) and strain (2–10%).[5,15]

1.1.1.1.1 Polypyrrole

One of the best known conductive organic polymers is PPy. This material is attractive due to its p-conjugated and heteroaromatic structures which produce high electrical conductivity (up to 50 S/cm)[16] and good chemical stability.[14]

Though, the π-conjugated structure is not enough for the observable conductivity, so that it is required the partial charge extraction from polymer backbone, which could be obtained in the process of a chemical or electrochemical redox reaction. In the reduced state the PPy polymers own the properties of an insulator, however, being oxidized there appear the positively charged particles on the polymer backbone (Figure 3), which cause the electrical conductivity.[14]

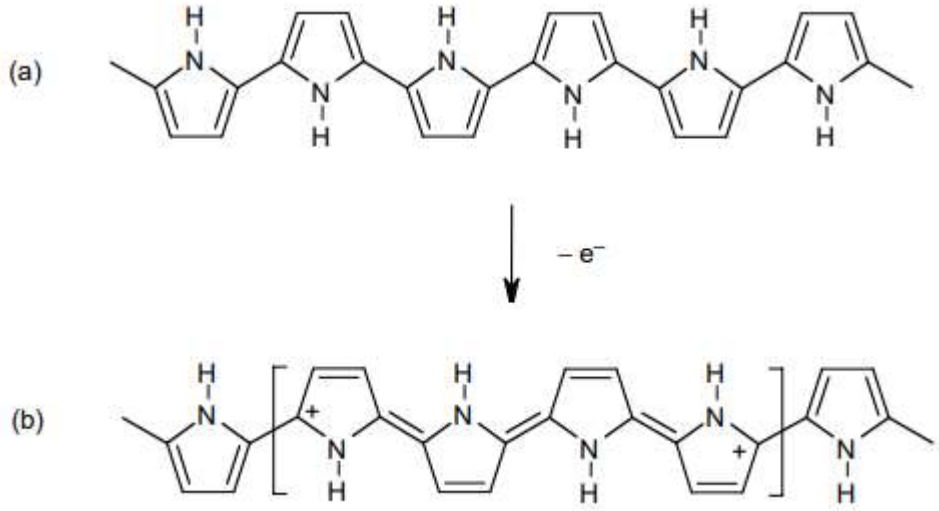


Figure 3. Oxidation of PPy. (a) Neutral form of PPy (b) Structure of oxidized PPy.[14]

In consequence, for the remaining of electroneutrality, the counterion from the surrounding absorb into the polymer during oxidation and are extracted in the process of reduction (Equation 1). Such ions replacement causes the change in the polymer volume.[17]

$$PPy°(AC) \rightleftarrows PPy^{+}(A^{-}) + C^{+} + e^{-}$$

$$\text{Reduced state} \rightleftarrows \text{Oxidized state}$$

Equation 1. Representation of PPy oxidation with cation driven neutralization, where $PPy^{0}(AC)$ represents neutral PPy polymer soaked in the ionic electrolyte, C^{+} indicates ejected cation and PPy^{+} (A^{-}) – the oxidized molecule of PPy with doped anion.[2]

The properties of conjugated polymer actuators are strongly depended on the synthesis conditions: reaction temperature and time, type of solvent and nature of doping counterions. The major part of PPy polymers is electrochemically polymerised, though there is another method of polymer preparation by chemical oxidation of pyrrole monomers.[18,19] In comparison to the alternative, electrochemical deposition leads to the higher conductivity, greater purity, more uniform layers and better mechanical properties.[20]

In addition to great electrochemical features, PPy has the positive biocompatibility profile, due to which, this polymer has received a great attention in the sphere of the biomedical implants.[21] The investigation of A. Fahlgren, C. Bratengeier et al has showed that PPy is tolerated by human primary osteoblast, moreover, doped with DBS PPy shows the most potent material surface for focal adhesion.[22] Another research produced by P.George, A.Lyckman et al was concentrated on the development of PPy for the future using of this polymer in the manufacture of neural prosthetics.[21]

1.1.1.2 Electrolytes

The choice of proper electrolyte is crucial for the properties of future IEAP actuators, since the efficiency of laminate bending depends on the several factors and features of electrolyte is one of them. Suitable for IEAP solvent must have high ionic conductivity (>10^{-4} S/cm), a large electrochemical window (>1 V), electrochemical and mechanical stability and ability to function in air. The polymer must be stable in the electrolyte solution in repeating redox reactions and ions should own high ionic mobility.[1,24]

Initially, aqueous salt solutions have been used as electrolytes for the IEAP actuators. Such systems had several significant disadvantages: high volatility, instability of electrolyte in open air, limited lifetime of actuators. Therefore, a new type of solvents known as ILs have been investigated for the replacement of the previous electrolytes.[1]

The volume change and displacement of the actuator are strongly dependent on the size and mobility of ions in the solvent, on the conductivity and concentration.[11] So that investigation of L.Bey, T.Jacobsen et al showed out that with an increase of electrolyte concentration, the expansion of polymer decreased.[23] In contrast, the average oxidation charge per chain increases proportionally to the increase of electrolyte concentration, showing the dual effect of the solvent dilution.[25]

The concentration and composition of electrolyte determinate not only the speed and displacement of actuator bending but also influence, whether actuation mechanism will be anion or cation driven. So that R.Kiefer, J.Martinez et al. by comparison the behaviour of trilayer actuators in four different electrolytes, have investigated that solvents with low dielectric constant and dipolar moment cannot break the ionic couple between doped ions and counterions inside the polymer chain and as a result cause the anion exchange.[26]

One more key characteristic of electrolyte is electrochemical stability. That could be found by certain voltage limits, where the inert behaviour of the solvent appears.[27] This electrochemical window (EW) (a term for indication the potential ranges within electrolyte remains stable) depends on the oxidative and reductive stability of the compound[27] and can be calculated as a difference of reduction and oxidation potentials.

1.1.1.2.1 Ionic liquids

Long ago the term “ionic liquid” was used for classical molten salts, which needed great energy input and consequently high temperatures for breaking the salt lattice. However, recently ILs are known as organic salts with a melting temperature below the boiling point

of water and as normal salts consist only of ions, being free of molecular solvents. Bigger interest is paid to ILs which stay liquid at room temperatures or even below and known as room temperature ILs (RTIL).[27,28]

The main method for ILs synthesis consists of two parts: preparation of the halide salt with necessary cation by alkylation and replacement of halide anion by required one in the process of anion metathesis. The properties of ILs depend on the nature of cations and ions, so that the major part of salts with low-melting point has ±1 charges on the ions. Furthermore, RTILs stay liquid at low temperatures due to large asymmetric ions with delocalized charged and reduced overall charge density. In Figure 4 and Figure 5 are depicted some commonly used ions in ILs.[27]

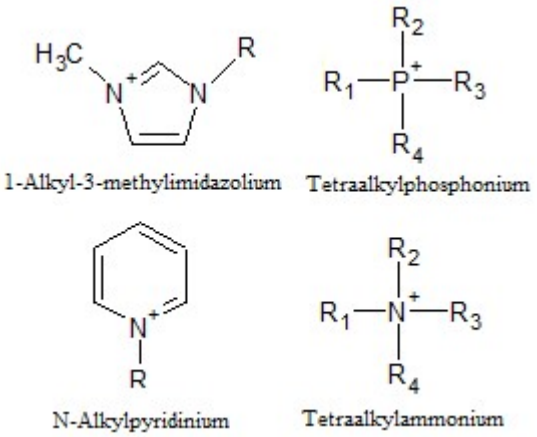


Figure 4. Commonly used ILs cations.[29]

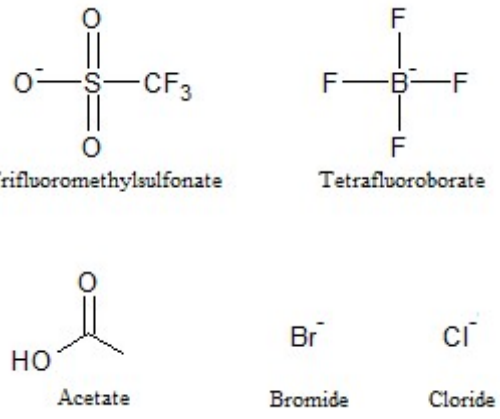


Figure 5. Commonly used ILs anions.[29]

The physicochemical properties of RTILs are similar to high temperature molten salts, however, some features like ion-ion interactions differs ILs as a separate class of compounds.[28] Among different unusual properties, such as thermal stability, high ion density, low melting point (below room temperature), such features as non-volatility and non-flammability make RTILs a great solution for safe electrolytes in fuel cells, capacitors and several electrochemical devices.[30]

However, considering ILs as an electrolyte for electrochemical studies, it is essential to know the conductivity and the electrochemical stability of the liquid. The resistance of the cation to reduction and the resistance of the anion to oxidation have the most effect on the EW of RTILs.[27] The conductivity of ILs is up to ~10 mS/cm[27] and average meaning of EW is between 2.0 and 6.0 V[29]. Though, it must be noted that the presence of impurities in solvent can change the potential ranges and shift the EW magnitude. The most common impurities

in RTILs are water and oxygen, which are easily dissolved from the air and have their impact on the electrochemical parameters.[27,30]

Owing to high intrinsic conductivities, large electrochemical windows, and negligible vapor pressures environmentally stable ILs can be used as solvent for EAP as an alternative to salt solutions.[24] So that in research work of W.Lu, A.Fadeev et al. the influence of 1-butyl-3-methylimidazolium hexafluorophosphate IL and solution of tetrabutylammonium hexafluorophosphate in propylene carbonate on the π-conjugated polymers have been compared. The investigation has showed that actuators soaked in IL have more stable charge ratio and displacement even after 5000 cycles, when the break of the polymer backbone in actuators with salt solution electrolytes has happened already after 2000 cycles.[1]

Although, IL are considered to be safe electrolytes, due to their low flammability and non-volatility, their toxic influence on the mammalian and bacterial cells does not allow to name these solvents as "green" and to use them as electrolytes in actuators for medical approaches.[31] So that S.Ruokonen, C.Sanwald et al. have checked the impact of ILs to human corneal epithelial cells and Vibrio fischeri bacteria and conclude that ILs can be divided into three groups conditionally to the mechanism of toxicity: cell membrane rupturing ILs, compounds that affect cell metabolism and liquids which influence both to the cell membrane and metabolism.[31] Later similar results have been confirmed by C.Sanwald, A.Robciuc et al., it was investigated that ILs do not affect a lot to the aliphatic amino acids (Leu, Ile, and Val), however, the concentrations of alanine and glycine in the cells have decreased proportionally to the toxicity of ILs. The only exceptions were two choline based ILs.[32]

That is the reason for the requirements in the new more biofriendly solvents for the electrolytes in IEAP actuators.

1.1.1.2.2 Deep eutectic solvents

Deep eutectic solvents (DES) could be defined as a eutectic mixture of several compounds, which melting point is lower than the melting temperature of each separate ingredient.[33] DESs are the new type of solvents, which could be divided into four types based on the mechanism of formation: [33,34]

1) Mixture of organic and metal salts (Cat^+X^- - $zMClx$)
2) Mixture of organic and hydrated metal salts (Cat^+X^- - $zMClx \cdot yH_2O$)
3) Mixture of organic salt and hydrogen bond donor (Cat^+X^- - zRZ)

4) Mixture of metal salt and hydrogen bond donor (MCl_x+RZ)

The main interest is paid to the DESs of the third type. In these solvents, the hydrogen-bond donor forms a complex with anion, causing the delocalization of the anion charge and as result, decrease in the melting point.[29] The research shows that two molecules of carboxylic acid or one molecule of dicarboxylic acid are needed to complex every chloride ion for a formation of eutectic.[35]

In contrast to RTIL, DES can be easily prepared by simple mixing of raw materials and stirring until the formation of homogeneous liquid.[34,36] Such synthesis is more energy efficient,[36] as it does not required anion exchange and long purification process, which are essential in the case of IL.[27]

More significant is the fact that DES of the third type could be formed from renewable, non-toxic, natural compounds what makes those solvents more biocompatible.[36] Additionally, such materials are not expensive, what derive a low cost of production.[34] For instance, (2-hydroxyethyl)trimethylammonium chloride also called as choline chloride (ChCl) is one of the most often used chemicals used for the preparation of DES.[37] It is known to be safe and biodegradable quaternary ammonium salt, which is used as provitamin and produced in large scales as animal feed.[34]

Majority of the DES have high viscosity at room temperature, which is caused by low mobility of free particles due to hydrogen bond connections, large ions and small void volumes.[37] The researches have revealed that the viscosity of DES (from 50 to 5000 cP)[35] are comparable to those detected with choline and carboxylates based IL (650-8500 cP).[38] Furthermore, the viscosity of DES, as well as of IL, follow the Arrhenius-like behaviour.[35] The potential of both IL and DES are temperature dependent and with heating the solvent, the ionic conductivity rises.[37]

In general, DES have various similar properties to RTIL, such as large EW (3.7 V),[39] non-volatility and non-flammability.[36] Additionally, DES are nonreactive with water, the synthesis is easy and cheap and for their production biodegradable and non-toxic compounds are used. Due to such parameters this new type of solvents could be used as a bio-friendly alternative electrolyte to RTIL.[35]

2 THE AIMS OF THE THESIS

The hypothesis of the current thesis was: could DESs be comparable alternatives to ILs electrolytes in IEAP actuators

The next aims have been obtained, during the research for proving the hypothesis:

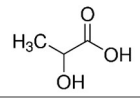
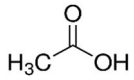
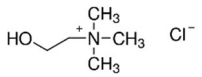
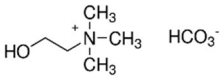
- Synthesis of IL ([Ch][LA]) and preparation of DES-is from [Ch]Cl and acetic or lactic acid, as the future electrolyte for the PPy actuators.
- Fabrication of IEAP actuators from commercial PVDF membrane, electrochemically deposited PPy electrodes and synthesized electrolytes.
- Characterization of received IEAP actuators by means of CV, actuation and mechanical properties.
- Comparison of actuators' performance in case of different ILs ([Ch][AC], [Ch][LA]) and DESs as electrolytes.

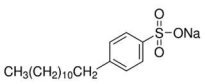
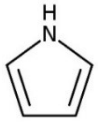
3 EXPERIMENTAL PART

3.1 MATERIALS AND METHODS

3.1.1 Materials

Table 1. Properties of the used chemicals.

Chemical name	MW (g/mol)	Mp (°C)	Bp (°C)	ρ (g/cm³)	Solubility	Hazards*	Physical form
Lactic acid 85%[40] 	90.08	53	122	1.206	In water: 1000 g/L	H315, H318	Viscous liquid
Acetic acid ≥99.8%[40] 	60.05	16.6	118.1	1.05	Miscible in water	H226, H290, H314	Colourless liquid
Choline chloride  **≥98%**[40]	139.62	302 – 305	-	-	In water 50 g/L	-	White solid
Choline bicarbonate  **~80%**[40]	165.19	-	-	1.17	Soluble in water	H315, H319, H335	Liquid

Sodium Dodecylbenzenesulfonate[40] 	348.48	204-207	100	1	In water: 0.8 g/L at 25 °C	H302, H315, H318	White solid
Pyrrole[40] 	67.091	23	129.7	0.967	In water: 10 g/L at 20 °C	H226, H301, H318, H332	Pale-yellow liquid

* H226 – Flammable liquid and vapour.

H290 – May be corrosive to metals.

H301 – Toxic if swallowed.

H302 – Harmful if swallowed

H314 – Causes severe skin burns and eye damage

H315 – Causes skin irritation.

H318 – Causes serious eye damage.

H319 – Causes serious eye irritation.

H332 – Harmful if inhaled.

H335 – May cause respiratory irritation.

PVDF membrane – porosity of 70%, pore size:0.45 um, thickness: 110 μm, Immobilon-P, Sigma-Aldrich

[Ch][AC] has been synthesised in IMS lab, the structure was confirmed by IR and 1H NMR, the water content in the IL was determined by Karl Fisher titration <5%.

3.1.2 Equipment

- IR spectrometer: Tensor 27 FTIR, Bruker, USA

- NMR spectrometer: Avance II, Bruker, USA (all NMR spectra in the current thesis has been measured and interpreted by Kaija Põhako-Esko)
- SEM: TM3000 Tabletop Scanning Electron Microscope, Hitachi, Japan
- Rotary evaporator: Rotavapor R-3, Büchi, Switzerland
- Vacuum pump: V-700, Büchi, Switzerland
- Vacuum controller: V-850, Büchi, Switzerland
- Low-temperature thermostat: Proline RP 1845, LAUDA-Brinkmann, USA
- Potentiostat/galvanostat: PARSTAT 2273 (Advanced electrochemical system), USA
- Laser distance meter: in-house set-up
- Vacuum drying oven: VO200, Memmert GmbH + Co. KG, Germany
- High vacuum atom sputter: Leica EM ACE600, Germany
- Digital multimeter: LCR Meter LCR200, EXTECH Instruments, China (Taiwan)
- Analytical balance: AB204-S/PH, Mettler Toledo, Switzerland
- Mechanical pipets: Biohit mLINE, Sartorius, Germany
- Digital ceramic magnetic stirrer hot plate: Arec.X, VELP Scientifica, Italy

3.1.3 Preparation of electrolytes

3.1.3.1 Synthesis of [Ch][LA]

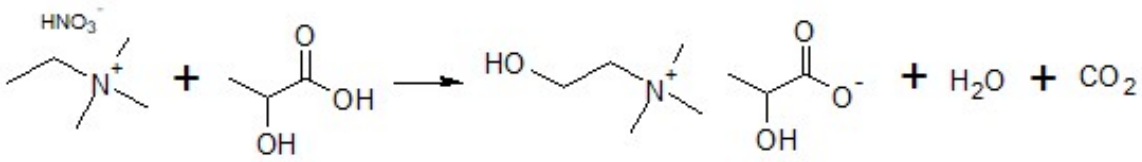


Figure 4. Reaction scheme for the synthesis of [Ch][LA].

10.324 g (0.05 mol) of 80% choline bicarbonate solution in water and 5.48 g (0.052 mol) of 85% mixture of lactic acid were separately dissolved in distilled water. Dissolved acid was added to the solution of choline bicarbonate dropwise. As a side product CO_2 releases during the synthesis (Figure 5). The produced mixture was stirred overnight at room temperature until the reaction was completed. The purification of synthesized IL from initial unreacted components was done by the method of liquid-liquid extraction with the usage of 20 ml of ethyl acetate. Using separation funnel the aqueous phase with IL was separated from the organic phase (Figure 6). The process has been repeated three times. After that, gathered organic phase was washed with 20 ml of distilled water, for fully collecting the left drops of IL. At the end of purification, the rotary evaporator was used for removing water from the

mixture. Finally, it was produced 9.894 g of viscose colourless liquid of [Ch][LA] with a yield of 98.9%. For the confirmation of the IL structure, the IR (Figure A1-2) and 1H NMR spectrometry have been done.

IR: 3233 cm^{-1} v(O-H); 3031 cm^{-1}, 2970 cm^{-1}, 2930 cm^{-1}, 2872 cm^{-1} v(C-H); 1589 cm^{-1} v(C=O); 1478 cm^{-1}, 1452 cm^{-1} v(C-N); 1373 cm^{-1} σ(O-H); 1119 cm^{-1}, 1085 cm^{-1}, 1031 cm^{-1} v(C-O); 922 cm^{-1} σ(C-O); 650 cm^{-1}, 532 cm^{-1} σ(C-H) (Figure A1)

1H NMR: 1H NMR (400 MHz, D_2O): δ (ppm) = 4,66 (s, 1H, O**H**), 3,82 (m, 2H, NC**H**$_2$), 3,27 (m, 2H, C**H**$_2$OH), 2,95 (s, 9H, N(C**H**$_3$)$_3$), 1,13 (m, 3H, C**H**$_3$).

Figure 5. Adding of dissolved lactic acid to choline bicarbonate.

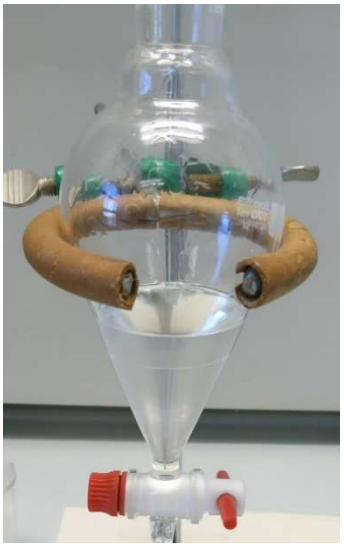


Figure 6. Produced liquid with two layers.

3.1.3.2 Preparation of DESs

[Ch]Cl (≥98% of purity) was mixed together with carboxylic acids in different concentrations. After that produced mixtures were left for seven days, as the process of [Ch]Cl dissolution in acids was quite slow. For the confirmation of the DES concentration, the NMR spectroscopy has been done. If [Ch]Cl was not completely dissolved in acid, then NMR analysis helped to determine the concentration of the compound in liquid and determine maximum solubility for [Ch]Cl. Since its results for some samples differed quite a lot from theoretical concentrations, one more set of samples has been done. This time for the complete blending, solutions were stirred for 24 hours and left for 3 more days, so that undissolved salt could precipitate on the bottom of vials. The NMR spectroscopy has been repeatedly done for the newly prepared DES-is. Samples with the closest concentration to the theoretical have been chosen for further experiments.

3.1.3.2.1 Preparation of DES from [Ch]Cl and acetic acid

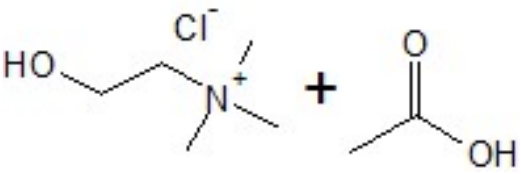


Figure 7. Preparation of DES from [Ch]Cl and acetic acid.

Table 2. Properties of prepared DES-is from [Ch]Cl and acetic acid.

Synthesis	Theoretical ratio	Mass of [Ch]Cl (g)	Mass of 99.8% acetic acid (g)	Experimental molar ratio for liquid phase from NMR	Physical form	Used in further experiments
[Ch]Cl:AA	1:2	2.6888	2.3162	1:2.17	Homogeneous solution of colourless liquid	Yes
[Ch]Cl:AA	1:1	3.4909	1.5007	1:1.84	Whitish liquid, due to presents of undissolved solid crystals	No
[Ch]Cl:AA	2:1	4.1058	0.8945	-	Heterogeneous solution, indivisible mixture of liquid and crystals	No
[Ch]Cl:AA	1:2	2.689	2.3773	1:1.86	Homogeneous solution of colourless liquid	No
[Ch]Cl:AA	1:1	3.4908	1.4968	1:1.65	Whitish liquid, due to presents of undissolved solid crystals	Yes

[Ch]Cl :AA	2:1	4.1048	0.8625	-	Heterogeneous solution, indivisible mixture of liquid and crystals	No

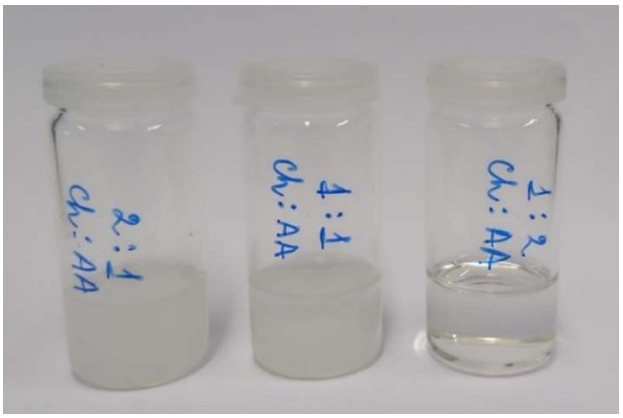


Figure 8. Prepared samples of DES-is [Ch]Cl :AA.

3.1.3.2.2 Preparation of DES from [Ch]Cl and lactic acid

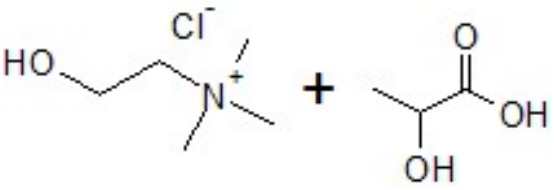


Figure 9. Preparation of DES from [Ch]Cl and lactic acid.

Table 3. Properties of prepared DES-is from [Ch]Cl and lactic acid.

Synthesis	**Theoretical ratio**	**Mass of choline chloride (g)**	**Mass of 85% lactic acid (g)**	**Experimental molar ratio for liquid phase from NMR**	**Physical form**	**Used in further experiments**
[Ch]Cl :LA	1:2	2.1788	3.3144	1:2.03	Homogeneous solution of colourless liquid	Yes
[Ch]Cl :LA	1:1	3.0438	2.2965	1:0.893	Homogeneous solution of colourless liquid	Yes

[Ch]Cl :LA	2:1	3.7696	1.6179	2:1.5625	Whitish liquid, due to presents of undissolved solid crystals	No
[Ch]Cl :LA	1:2	2.1784	3.2916	1:1.87	Homogeneous solution of colourless liquid	No
[Ch]Cl :LA	1:1	3.0433	2.3045	1:0.862	Homogeneous solution of colourless liquid	No
[Ch]Cl :LA	2:1	3.7703	1.4228	2:1.504	Whitish liquid, due to presents of undissolved solid crystals	Yes

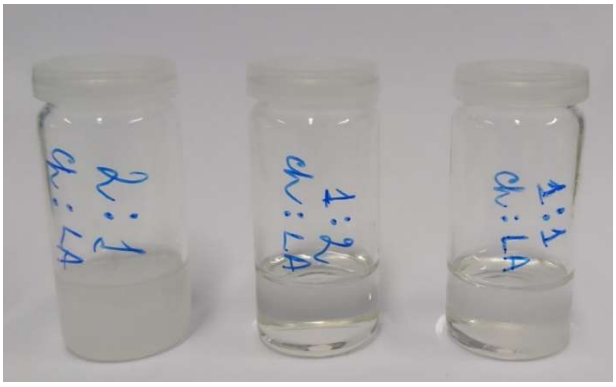


Figure 10. Prepared samples of DES-is [Ch]Cl:LA.

3.1.4 Preparation of actuators

For increasing conductivity, the PVDF membrane was coated with a thin gold film of 20 nm by the usage of high vacuum atom sputtering.

The main working surface of the actuators – PPy layer was simultaneously electrochemically deposited on the earlier prepared membrane of PVDF covered with gold. The CP was electrochemically synthesized from monomer and 0.2 M NaDBS solution in a mix of water and ethylene (50:50 v/v.%), which was prepared in advance. 16,728 g of 0.2 M NaDBS and 0.7996 g of pyrrole were added to the 240 ml of 50% water-ethylene glycol solution.

For the constant current source potentiostat/galvanostat PARSTAT 2273 was used. The polymerization was held for 10000 seconds (Figure A3) at current density 0.1 mA/cm2 at

temperature -23°C. The electrochemical synthesis of PPy was carried out in a cell pictured in Figure 11-12.

The produced films were washed with distilled water and 99.8% ethanol, after what they were dried in a vacuum oven at room temperature at least for 24 hours. The prepared PPy actuators were cut into 3x14 mm strips and held in electrolytes for a minimum of 72 hours.[41]

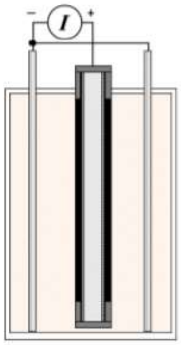


Figure 11. Schematics of electrochemical synthesis

Figure 12. Photo of polymer electrochemical synthesis[41]

3.1.5 Electromechanical characterisation of PPy actuators

Following parameters were determined for the prepared actuators:

- Maximum strain difference
- Charge efficiency
- Frequency response

Maximum strain difference is one of the parameters for the characterisation the properties of obtained PPy actuators. For finding out the meaning of this parameter the cyclovoltamperometric measurements have been done and during the same experiment, actuation was measured.

2 mm of the actuator were clutched between gold contacts allowing the second part of the actuator to move in the air. The bending of actuators was caused by CV triangular signals in the range of -1 and 1 V made by PARSTAT 2273 potentiostat and measured by a laser displacement sensor. Five circles have been recorded by directing laser in one point at 5 mm from the clutched end with scan rates of 5 and 50 mV/s.

From the obtained results the maximum strain differences (ε) have been calculated by equation 2:

$$\varepsilon = \frac{2DW}{L^2+D^2} \quad (2)$$

where D is half of the peak to peak displacement from graph, W is the thickness of the actuator, which was measured in advanced by a micrometre, and L is the distance from the fixed end of the actuator to the point, where measurements have been done.[42]

The charge-efficiency is another parameter for actuator characterization, its unit is (%·Coulomb^{-1}·cm^2). It was calculated as division of received strain difference (%) by charge density (Coulomb/cm^2).

Additionally, the frequency response of the actuators was characterized. It was done by a mirrored logarithmic sweep sine signal from 0.001 Hz to 400 Hz, with the amplitude of ±1 V.

For determination the structure of fabricated actuators the scanning electron microscopy (SEM) images of the cross-sections have been done. A few samples were broken in the liquid nitrogen and sputtered by 5 nm layer of gold. After that the SEM images of the best sample have been done by the usage of a Hitachi TM3000 microscope (acceleration voltage of 15 kV, back-scattered electron detector) with 800- and 7000-times magnification.

All measurements have been carried out under ambient conditions (26.5 RH%, 24.6°C, normal atmospheric pressure).

3.2 RESULTS AND DISCUSSION

3.2.1 Bending efficiency of actuators

The bending of actuators accompanied with various type of choline based electrolytes: [Ch][AC] (mp: 80°C) and [Ch]Cl:AA (mp below room temperature), [Ch][LA] (mp: -72.9°C) and [Ch]Cl:LA (mp: -77.7°C)[43] has been measured with scan rate 5mV/s and 50mV/s. The obtained results are presented in the Table 4. Every actuator, where DES have been used as electrolyte, has produced some displacement. It is possible to suppose that ions in DES have enough high mobility for being relocated into the porous structure of PPy. All tested actuators had dominant cation-driven actuation mechanism.

Table 4. The strain difference and charge-efficiency parameters for actuators with different electrolytes.

Electrolyte	Strain difference (%)		Charge-efficiency (%·cm^2/Coulomb)	
	5 mV/s	50 mV/s	5 mV/s	50 mV/s
[Ch][AC]	0.38	0.21	6.47	8.41
[Ch][LA]	0.27	0.18	5.61	10.46
[Ch]Cl:AA (1:2)	0.49	0.25	7.45	4.31
[Ch]Cl:AA (1:1)	0.37	0.19	5.98	8.56
[Ch]Cl:LA (1:2)	0.12	0.05	7.48	9.48
[Ch]Cl:LA (1:1)	0.12	0.07	12.54	14.38
[Ch]Cl:LA (2:1)	0.10	0.05	17.10	14.63

The strain difference and charge-efficiency measurements have shown that actuators soaked in DES were comparable or even exceed the performance of actuators with ILs. The highest strain efficiency was obtained by actuators with [Ch]Cl:LA DES electrolytes, what reveals interesting tendency, charge-efficiency is inverse to the strain-difference.

3.2.2 Frequency response

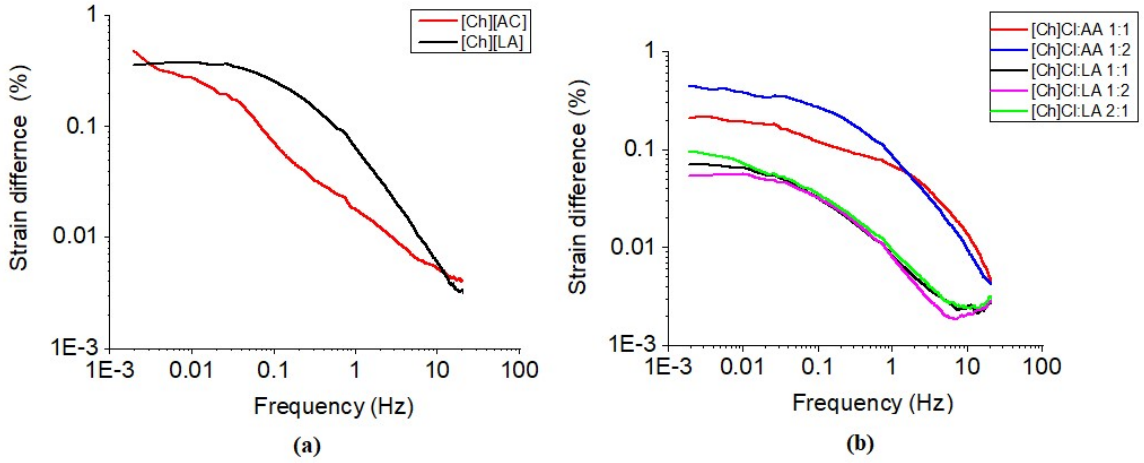


Figure 15. Frequency response of actuators. (a) Frequency response of actuators with ionic liquids electrolytes. (b) Frequency response of actuators with DES electrolytes.

Frequency response plot of actuators with DES electrolytes (Table 15.b) shows that actuators with DES electrolytes formed from acetic acid has higher strain difference in compresence with actuators with DES electrolytes formed from lactic acid with the same frequencies. Such behaviour could be explained by the size of the acids' molecules. Since acetic acid molecules are smaller than molecules of lactic acid (in comparisons to acetic acid, lactic acid molecules have longer alkyl chain and one additional hydroxyl group), they form holes of bigger dimension for the choline cations movement,[35] consequently the bigger displacement at higher frequencies could be obtained. In contrast, in case of the actuators with IL electrolytes (Figure 15.a) [Ch][LA] exceed the results of [Ch][AC] electrolytes.

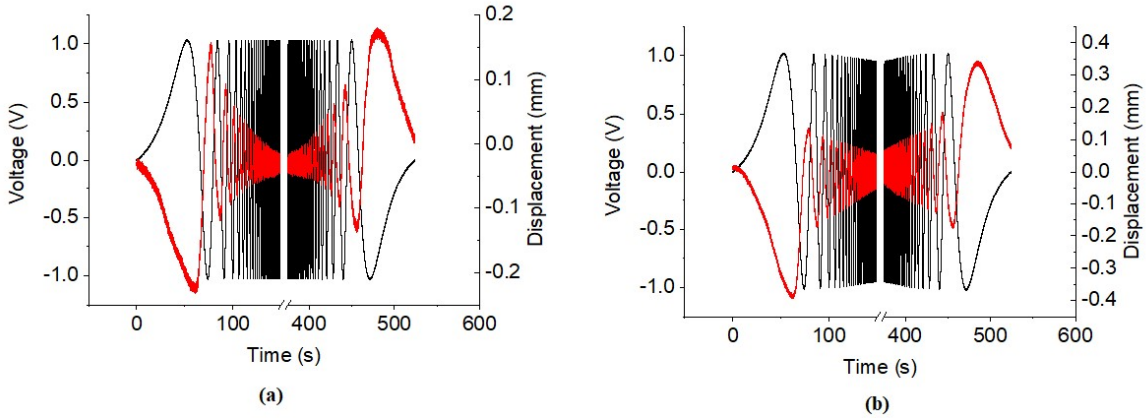


Figure 16. Frequency response of actuators. (a) Frequency response of actuator with [Ch][AC] IL electrolytes. (b) Frequency response of actuators with [Ch]Cl:AA DES electrolyte with concentration 1:2.

The frequency response graph (Figure 16) shows that even though actuators were excited by 400Hz, they did not lose their actuating properties. From the plot can be seen, that actuators with [Ch]Cl:AA electrolyte have shown comparable results to actuators with [Ch][AC] ionic liquid electrolyte. The frequency response graphs of actuators with other electrolytes can be seen in Appendix (Figure A4).

3.2.3 Cyclovoltammetry

Cyclic voltammograms (CVs) of actuators measured simultaneously at the 3rd cycle is shown in Figures 13-14. The CV plots reveal that actuators with DES electrolytes exhibit better capacitor like behaviour than actuators with IL electrolytes. It can be seen by increase in current, which actuator can conduct.

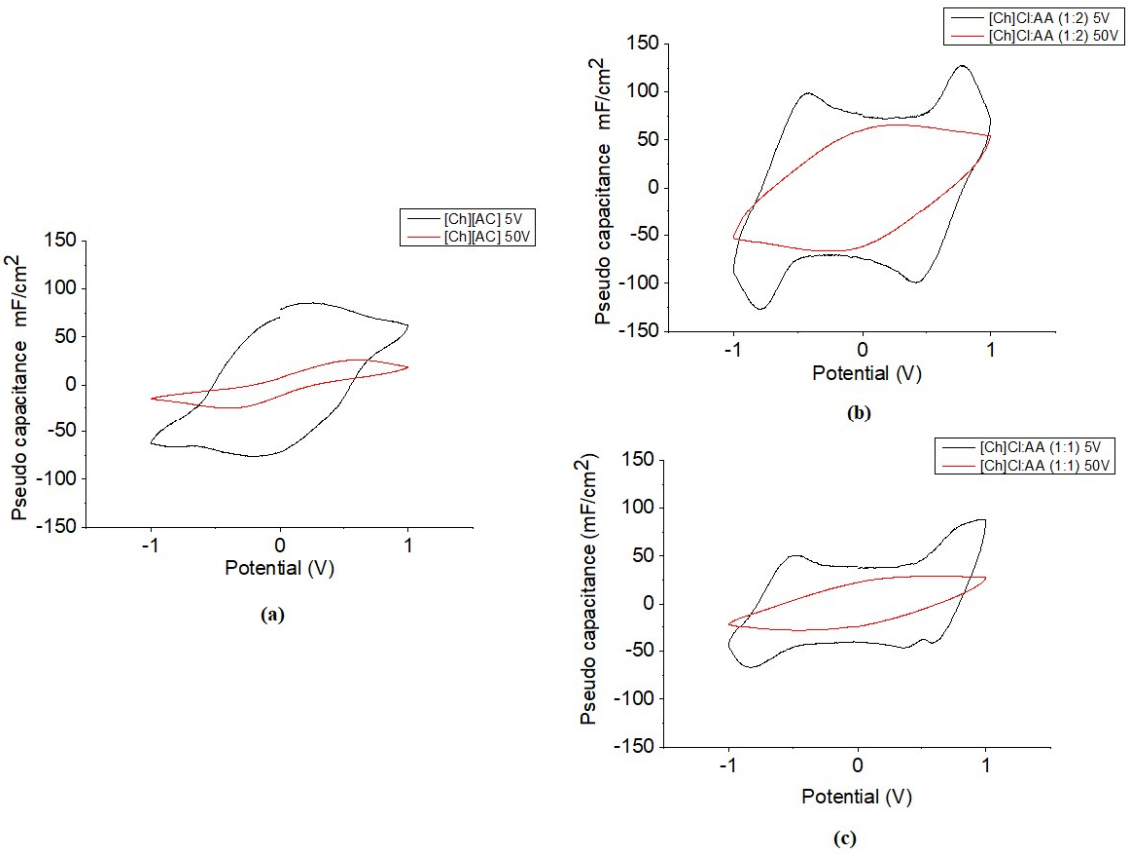


Figure 13. CV of actuators with scan rate 5V and 50V. (a) CV graph of actuators with [Ch][AC] IL electrolyte. (b) CV graph of actuators with [Ch]Cl:AA electrolyte with concentration 1:2. (c) CV graph of actuators with [Ch]Cl:AA electrolyte with concentration 1:1.

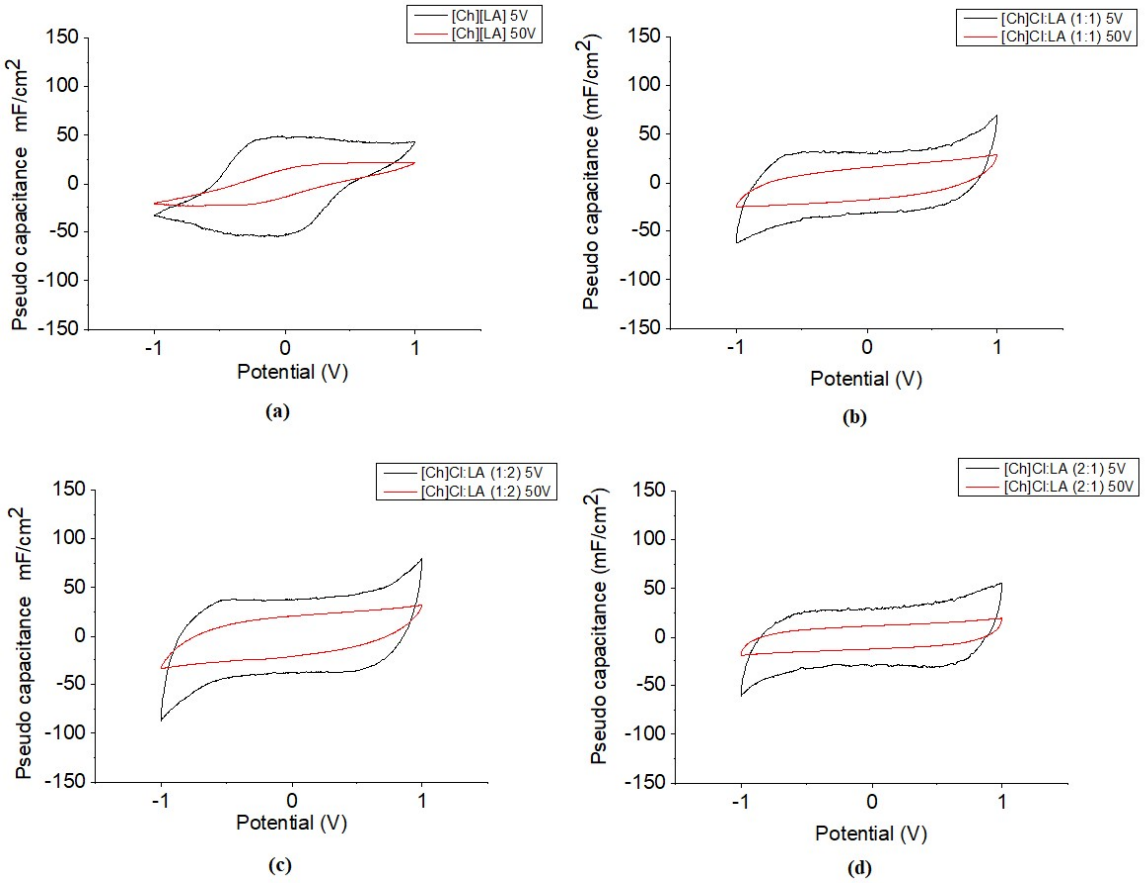


Figure 14. CV of actuators with scan rate 5V and 50V. (a) CV graph of actuator with [Ch][LA] IL electrolyte. (b) CV graph of actuators with [Ch]Cl:LA electrolyte with concentration 1:1. (c) CV graph of actuators with [Ch]Cl:LA electrolyte with concentration 1:2. (d) CV graph of actuators with [Ch]Cl:LA electrolyte with concentration 2:1.

Both strain difference (Table 4) and cyclic voltammetry (Figure 13-14) have proved interesting relationship between amount of the salt in the DES and the conductivity of electrolytes. The graphs show that the lower the molar concentration of [Ch]Cl in the ratio with acid the better results could be obtained. Such unusual tendency could be explained by high viscosity of DESs, which is affected by the nature and amount of the salt. [35] Since it is known that the conductivity is inverse to the viscosity, the more fluid electrolytes are preferred. With the increase in the salt concentration, rises the viscosity of the solvent and consequently decreases the conductivity of the liquid.

Similar result has been obtained by J.Martinez, T.Otero and E.Jager in 2014.[25] Such phenomena was explained by decrease of free water molecules in solution in response to increase of electrolyte concentration. With decrease of free water, the osmotic pressure drops and as a result, reaction rate and plasticity become lower.[25]

3.2.4 Structure of actuators

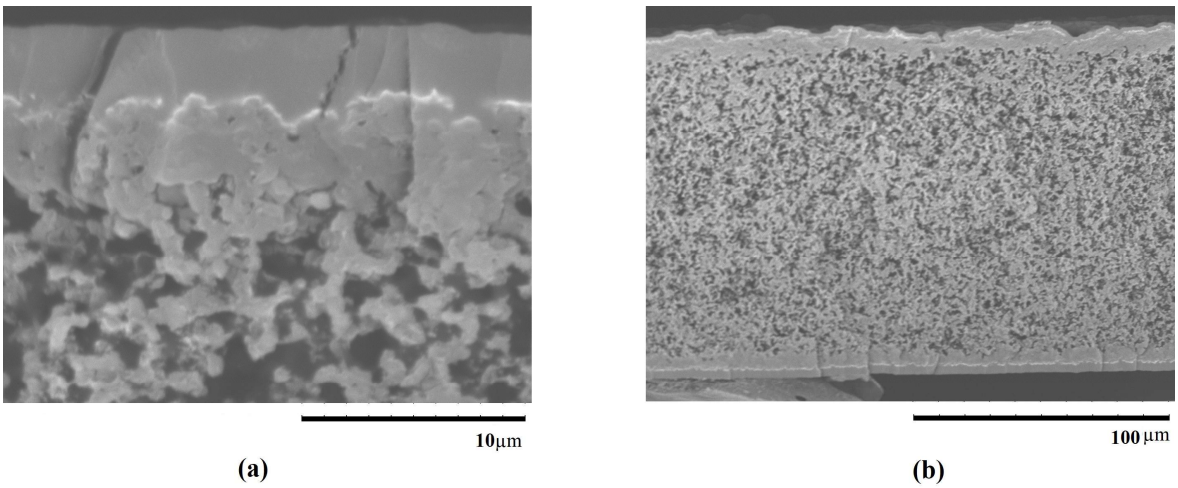


Figure 17. SEM pictures of PPy actuator with [Ch][AC] electrolyte in cross section. (a) SEM with 7000 -times magnification (b) SEM with 800 -times magnification.

In the Figure 17 are depicted the cross section of PPy actuator, which reviles the porous structure of PVDF membrane. From the SEM pictures can be seen the uniform layer of PPy, which in comparison to the membrane (110 μm) has thin thickness of ~2 μm. The structure of fabricated actuator corresponds to the theoretical expectations.

SUMMARY

The main goal and targeted aims of this work have been obtained. IEAP with different types of choline-based electrolytes have been prepared and their ability to generate movement has been checked.

The fabricated PPy actuators with DES electrolytes have produced bending displacement and gave comparable results to their analogues with IL electrolytes.

The behaviour of produced IEAP actuators has been electrochemically characterised and compared. Actuators with both types of electrolytes (IL and DES) have the same cation driven mechanism of actuation. They could sustain high frequencies and continue bending even after 400 Hz. Furthermore, actuators with new type of solvents have showed more capacitor-like behaviour.

It is possible to conclude that the properties and effectiveness of actuator are depend on the nature and concentration of electrolyte and therefore, more research is required.

The results obtained in this work are significant for the area of biomedical application of actuators, since the new type of electrolytes makes them safer for use. Though, the influence of DESs should be checked in other types of actuators. The upcoming works should also investigate the reason, why actuators with DES electrolytes show more capacitor like behaviour than their analogues with ILs.

The main conclusion that could be drawn is that DES can be alternative electrolyte to ILs in IEAP.

ACKNOWLEDGEMENTS

I would like to express appreciation to my supervisors Fred Elhi and Kaija Põhako-Esko for this interesting topic, for their guidance and support during my research.

In addition, I would like to tank IMS Lab in the University of Tartu for nice working atmosphere and people, who attended during my project presentation for their comments and advice.

REFERENCES

1. Lu, W. *et al.* Use of Ionic Liquids for pi -Conjugated Polymer Electrochemical Devices. *Science.* **983**, 983–987 (2002).
2. Smela, E. Conjugated Polymer Actuators for Biomedical Applications. *Adv. Mater.* **15**, 481–494 (2003).
3. Wang, T. *et al.* Electroactive polymers for sensing. *Interface Focus* 1–19 (2016).
4. *Electroactive Polymers for Robotic Applications*. *Electroactive Polymers for Robotic Applications* (Springer, 2007).
5. Lafontaine, S. R. *et al.* Artificial Muscle Technology: Physical Principles and Naval Prospects. *IEEE J. Ocean. Eng.* **29**, 706–728 (2004).
6. Bar-Cohen, Y. *Electroactive Polymers as Artificial Muscles – Reality and Challenges*. (AIAA Copyright, 2001).
7. Baughman, R. H. Conducting polymer artificial muscles. *Synth. Met.* **78**, 339–353 (1996).
8. Alici, G. & Higgins, M. J. Stiffness characterisation of microcantilevers based on conducting polymers. *Smart Struct. Devices, Syst. IV* **7268**, 726806 (2008).
9. Mirvakili, S. M. & Hunter, I. W. Artificial Muscles : Mechanisms , Applications , and Challenges. *Adv. Mater.* **30**, 1–28 (2018).
10. Masurkar, N., Jamil, K. & Arava, L. M. R. Environmental Effects on the Polypyrrole Tri-layer Actuator. *Actuators* **6**, 17 (2017).
11. Cortés, M. T. & Moreno, J. C. Artificial muscles based on conducting polymers. *e-Polymers* 13 (2003).
12. Jager, E. W. H., Smela, E. & Inganas, O. Microfabricating conjugated polymer actuators. *Science (80-.).* **290**, 1540–1545 (2000).
13. Le, T. H., Kim, Y. & Yoon, H. Electrical and electrochemical properties of conducting polymers. *Polymers (Basel).* **9**, (2017).
14. Skotheim, T. A. & Reynolds, J. R. *Conjugated Polymers: Processing and Applications*. (CRC Press Taylor & Francis Group, 2007).
15. Spinks, G. M., Liu, L., Wallace, G. G. & Zhou, D. Strain response from polypyrrole actuators under load. *Adv. Funct. Mater.* **12**, 437–440 (2002).

16. Coldea, A., Turcu, R., Bot, A. & Brie, M. The Temperature Dependence of the Electrical Conductivity of Polypyrrole Films Doped with Different Counterions. *Rom. Reports Phys.* **52**, 127–138 (2000).

17. Otero, T. F. & Sansiñena, J. M. Artificial muscles based on conducting polymers. *Bioelectrochemistry Bioenerg.* **38**, 411–414 (1995).

18. Madden, J. D. Polypyrrole actuators: Properties and initial applications. *Electroactive Polymers for Robotic Applications: Artificial Muscles and Sensors* 121–152 (2007).

19. Myers, R. E. Chemical oxidative polymerization as a synthetic route to electrically conducting polypyrroles. *J. Electron. Mater.* **15**, 61–69 (1986).

20. Gvozdenovic, M., Jugovic, B., Stevanovic, J. & Grgur, B. Electrochemical synthesis of electroconducting polymers. *Hem. Ind. Ind.* **68**, 673–684 (2014).

21. George, P. M. *et al.* Fabrication and biocompatibility of polypyrrole implants suitable for neural prosthetics. *Biomaterials* **26**, 3511–3519 (2005).

22. Fahlgren, A. *et al.* Biocompatibility of polypyrrole with human primary osteoblasts and the effect of dopants. *PLoS One* **10**, 1–17 (2015).

23. Bay, L., Jacobsen, T. & Skaarup, S. Mechanism of Actuation in Conducting Polymers: Osmotic Expansion. *J. Phys. Chem.* 8492–8497 (2001).

24. Tsuda, T. & Hussey, C. L. Electrochemical Applications of Room-Temperature Ionic Liquids. *Electrochem. Soc. Interface* 42–49 (2007).

25. Martinez, J. G., Otero, T. F. & Jager, E. W. H. Effect of the electrolyte concentration and substrate on conducting polymer actuators. *Langmuir* **30**, 3894–3904 (2014).

26. Kiefer, R. *et al.* Polymeric actuators : Solvents tune reaction-driven cation to reaction-driven anion actuation. *Sensors Actuators B. Chem.* **233**, 328–336 (2016).

27. Wasserscheid, P. & Welton, T. *Ionic Liquids in Synthesis*. *Synthesis* (Wiley-VCH Verlag GmbH & Co. KGaA, 2008).

28. Galiński, M., Lewandowski, A. & Stepniak, I. Ionic liquids as electrolytes. *Electrochim. Acta* **51**, 5567–5580 (2006).

29. Freemantle, M. *An Introduction to Ionic Liquids*. (RSCPublishing, 2010).

30. Ohno, H. *Electrochemical Aspects of Ionic Liquids*. (A JOHN WILEY & SONS, INC., PUBLICATION, 2011).

31. Ruokonen, S. K. *et al.* Correlation between Ionic Liquid Cytotoxicity and Liposome–Ionic Liquid Interactions. *Chem. - A Eur. J.* **24**, 2669–2680 (2018).

32. Sanwald, C., Robciuc, A., Ruokonen, S. K., Wiedmer, S. K. & Lämmerhofer, M. A combined targeted/untargeted LC-MS/MS-based screening approach for mammalian cell lines treated with ionic liquids: Toxicity correlates with metabolic profile. *Talanta* **197**, 472–481 (2019).

33. Kudłak, B., Owczarek, K. & Namieśnik, J. Selected issues related to the toxicity of ionic liquids and deep eutectic solvents—a review. *Environ. Sci. Pollut. Res.* **22**, 11975–11992 (2015).

34. Smith, E. L., Abbott, A. P. & Ryder, K. S. Deep Eutectic Solvents (DESs) and Their Applications. *Chem. Rev.* (2014).

35. Abbott, A. P., Boothby, D., Capper, G., Davies, D. L. & Rasheed, R. K. Deep Eutectic Solvents formed between choline chloride and carboxylic acids: Versatile alternatives to ionic liquids. *J. Am. Chem. Soc.* **126**, 9142–9147 (2004).

36. Ruß, C. & König, B. Low melting mixtures in organic synthesis – an alternative to ionic liquids ? *Green Chem.* 2969–2982 (2012).

37. Zhang, Q., Vigier, K. D. O., Royer, S. & Jerome, F. Deep eutectic solvents : syntheses , properties and applications. *Chem. Soc. Rev.* 7108–7146 (2012).

38. Fukaya, Y., Iizuka, Y., Sekikawa, K. & Ohno, H. Bio ionic liquids: Room temperature ionic liquids composed wholly of biomaterials. *Green Chem.* **9**, 1155–1157 (2007).

39. Cruz, H., Jordão, N. & Branco, L. C. Deep eutectic solvents (DESs) as low-cost and green electrolytes for electrochromic devices. *Green Chem.* **19**, 1653–1658 (2017).

40. Sigma-Aldrich. Available at: https://www.sigmaaldrich.com/finland.html. last visit: 20.05.2019

41. Temmer, R. *Electrochemistry and novel applications of chemically synthesized conductive polymer electrodes*. (2014).

42. Sugino, T., Kiyohara, K., Takeuchi, I., Mukai, K. & Asaka, K. Actuator properties of the complexes composed by carbon nanotube and ionic liquid: The effects of additives. *Sensors Actuators, B Chem.* **141**, 179–186 (2009).

43. Francisco, M., González, A. S. B., García De Dios, S. L., Weggemans, W. & Kroon, M. C. Comparison of a low transition temperature mixture (LTTM) formed by lactic

acid and choline chloride with choline lactate ionic liquid and the choline chloride salt: Physical properties and vapour-liquid equilibria of mixtures containing water and ethanol. *RSC Adv.* **3**, 23553–23561 (2013).

Appendix

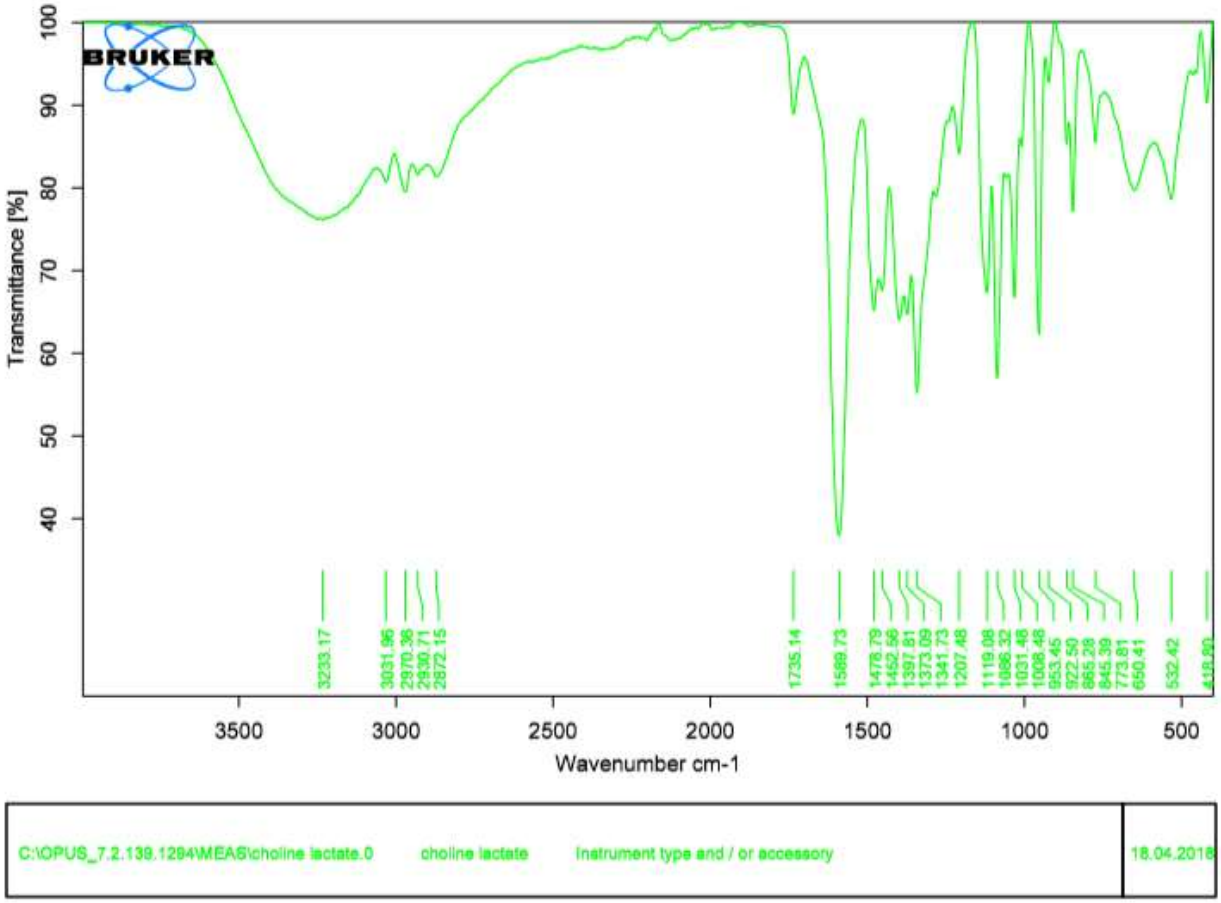


Figure A1. IR spectrum of synthesised [Ch][LA] ionic liquid.

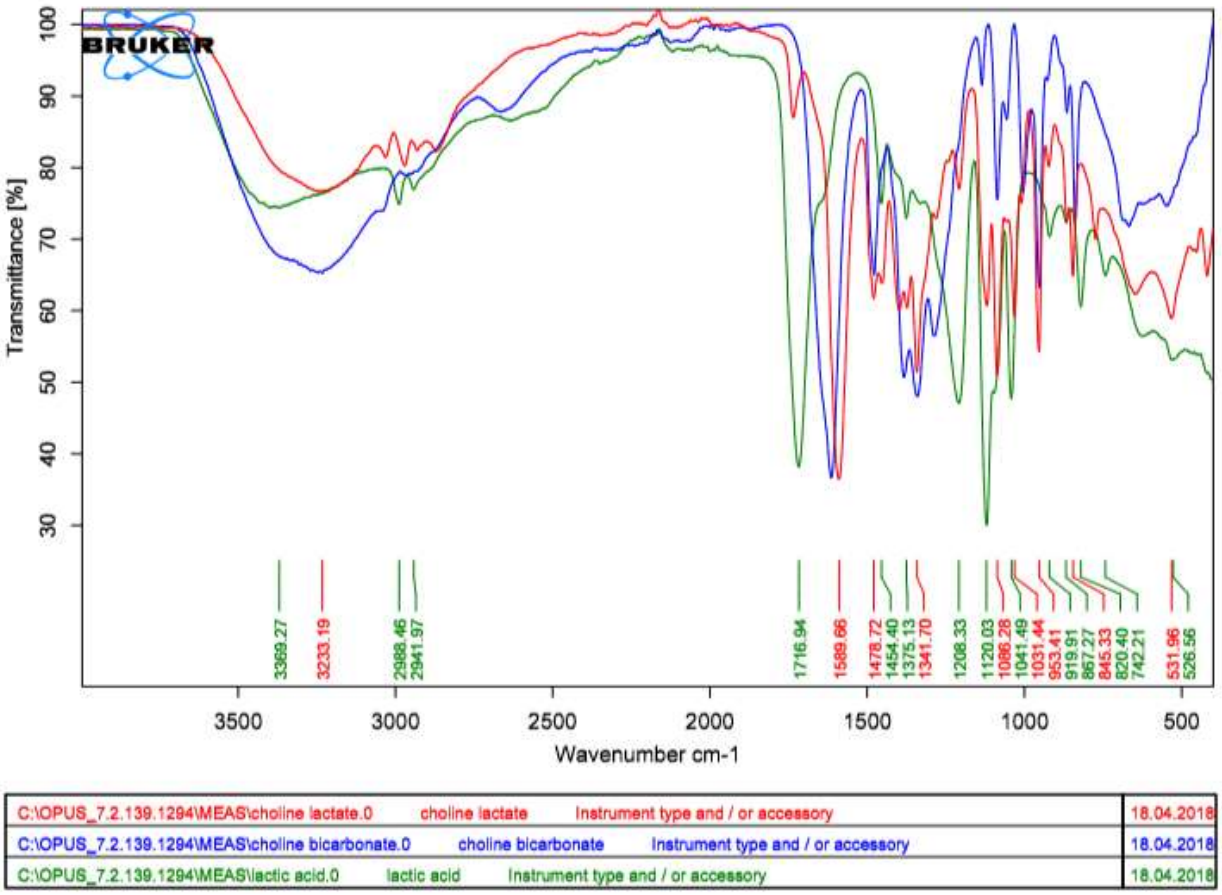


Figure A2. IR spectrum of synthesised [Ch][LA] ionic liquid and initial compounds.

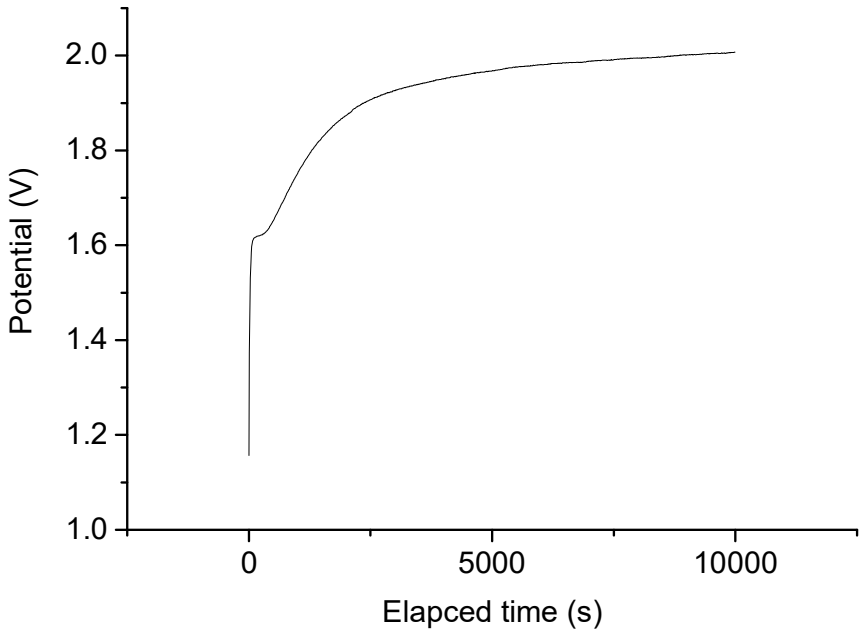


Figure A3. Chronopotentiogram of the electrochemical synthesis for PPy-PVDF actuators

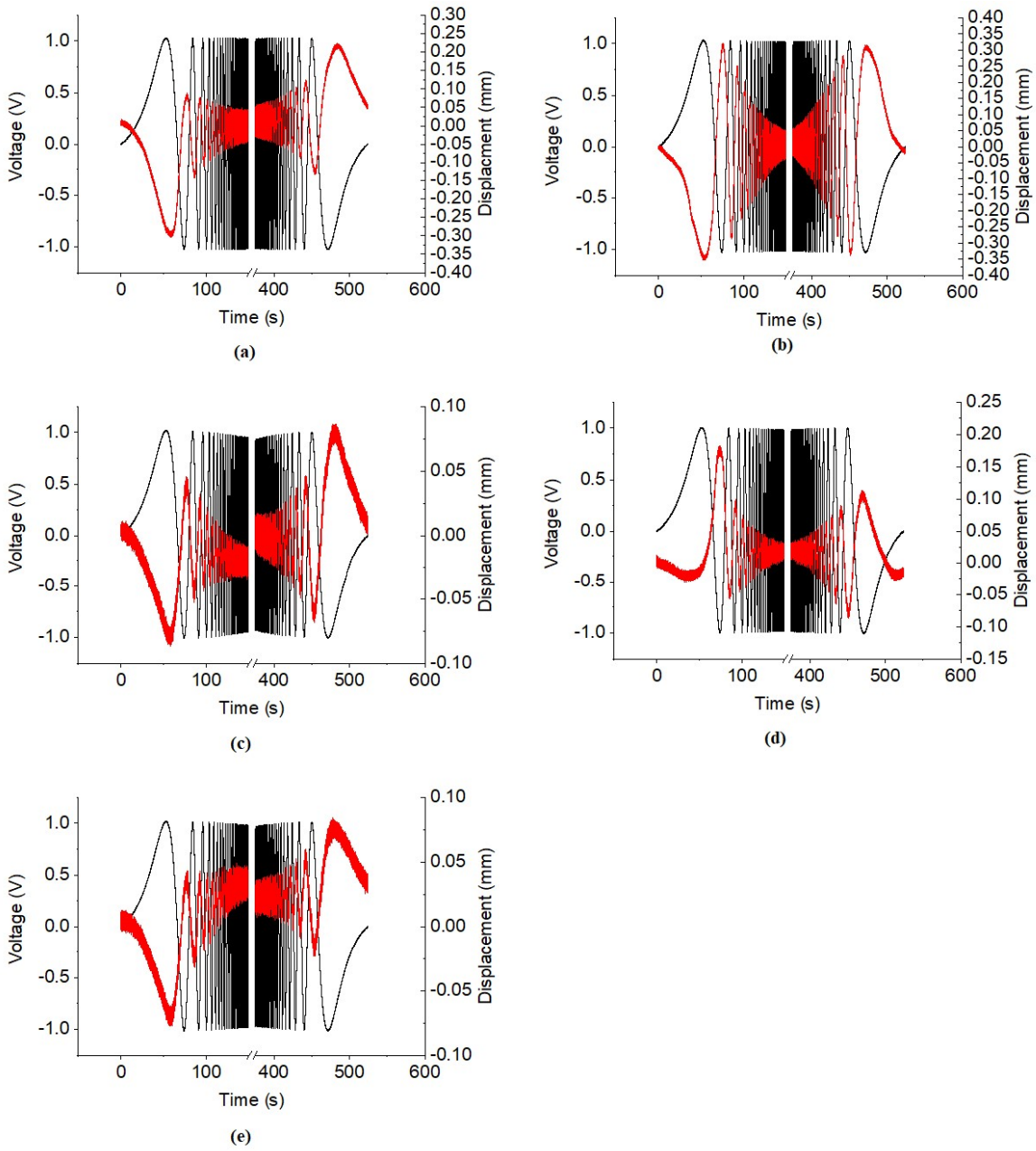


Figure A4. Frequency response of actuators. (a) Frequency response of actuator with [Ch]Cl:AA DES electrolyte with concentration 1:1 (b) Frequency response of actuators with [Ch][LA] IL electrolyte (c) Frequency response of actuators with [Ch]Cl:LA DES electrolyte with concentration 1:1 (d) Frequency response of actuators with [Ch]Cl:LA DES electrolyte with concentration 1:2 (e) Frequency response of actuators with [Ch]Cl:LA DES electrolyte with concentration 2:1.

NON-EXCLUSIVE LICENCE TO REPRODUCE THESIS AND MAKE THESIS PUBLIC

I, _____Jelena Volobujeva_____,

(*author's name*)

1. herewith grant the University of Tartu a free permit (non-exclusive licence) to

reproduce, for the purpose of preservation, including for adding to the DSpace digital archives until the expiry of the term of copyright,

Deep Eutectic Solvents as Electrolytes in Ionic Electromechanically Active Polymer Actuators_____

_____,

(*title of thesis*)

supervised by_____Fred Elhi, Kaija Põhako-Esko_____.

(*supervisor's name*)

2. I grant the University of Tartu a permit to make the work specified in p. 1 available to the public via the web environment of the University of Tartu, including via the DSpace digital archives, under the Creative Commons licence CC BY NC ND 3.0, which allows, by giving appropriate credit to the author, to reproduce, distribute the work and communicate it to the public, and prohibits the creation of derivative works and any commercial use of the work until the expiry of the term of copyright.

3. I am aware of the fact that the author retains the rights specified in p. 1 and 2.

4. I certify that granting the non-exclusive licence does not infringe other persons' intellectual property rights or rights arising from the personal data protection legislation.

Jelena Volobujeva

20/05/2019